

PREFACE

The present volume of *Inorganic Syntheses* continues the pattern of the last three volumes in the series, namely, specific thematic chapters along with other contributions that together reflect the diversity of inorganic synthetic activities in modern research.

The five chapters in this volume are arranged in a rough order of increasing complexity for the compounds described. Chapter 1 is a collection of syntheses for main group compounds, some interesting in their own right and others primarily for their use in metal complexes. Chapter 2 details procedures for largely mononuclear organometallic and coordination complexes, with central elements ranging across the periodic table and with a wide variety of ligand types. In contrast, Chapter 3 has a specific focus on transition metal compounds containing carbonyl ligands. Chapter 4 illustrates an explosively developing research theme in which the cyanide ligand is used as a linking agent in the assembly of polynuclear metal complexes with the purpose, for example, of achieving unique magnetic properties. Finally, procedures for other types of polynuclear and cluster compounds are displayed in Chapter 5. The articles in this volume will provide tested syntheses of compounds targeted for ongoing research. However, I trust, as in my own experience with *Inorganic Syntheses*, that they also will stimulate new research ideas, the results of which will serve to nurture future volumes in the series.

A volume of this sort does not happen without the contributions of many people, first and foremost, of course, the submitters and the checkers of the individual articles. I appreciate their patience when progress appeared to be slow and their quick responses when urgency was requested. Several individuals deserve explicit acknowledgment for their critical support of this project: Heinrich Vahrenkamp for his insight and effort in soliciting the cyanide-related syntheses in Chapter 4; Herb Kaesz for his interest in involving me with *Inorganic Syntheses*, initially with Volume 26, and for his sharp editorial eye regarding many articles that appear here; Marcetta Darensbourg for her experienced advice and counsel throughout the process of planning and assembling this volume; Stan Ching for his prompt and efficient handling of the manuscripts as they were submitted; and Julie Sides and Maureen Buxton for their truly invaluable secretarial assistance. I thank also the members of the Editorial Board for their many useful comments and suggestions regarding the submitted manuscripts.

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7. UNSYMMETRIC TRIPOD LIGANDS RELATED TO TRIS(PYRAZOL-1-YL)METHANE

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Tripodal ligands with a bridgehead carbon atom have assumed an important role in coordination and organometallic chemistry. Of particular interest are tris(pyrazol-1-yl)methanes,¹ isoelectronic with widely used tris(pyrazol-1-yl)borates. Unsymmetric ligands closely related to tris(pyrazol-1-yl)methane have been reported,^{2,3} and their lower symmetry is useful in a range of applications,²⁻⁶ including spectroscopic studies,^{3,4} and studies of isomerism^{2,5} and cycloplatination reactions.^{2b,5d} Symmetric tris(pyridin-2-yl)methane as a ligand has also been widely studied,⁷ and we describe here the facile syntheses of an unsymmetric mixed pyrazole/pyridine tripod ligand bis(pyrazol-1-yl)(pyridin-2-yl)methane, (pz)₂(py)CH, and closely related bis(pyrazol-1-yl)(*N*-methylimidazol-2-yl)methane, (pz)₂(mim)CH (see Fig. 1). These ligands contain heterocycles with closely related but different donor properties,^{4a,6,8} and subtle differences in donor group geometries presented to the metal center in complexes.^{4a} The synthetic strategy developed by Peterson is employed, relying on the condensation of bis(pyrazol-1-yl)methanone, (pz)₂C=O, with aldehydes, R(H)C=O, to give (pz)₂(R)CH and carbon dioxide.⁹ The syntheses of the precursor reagents (pz)₂C=O^{9c} and *N*-methylimidazole-2-carbaldehyde {(mim)(H)C=O},¹⁰ developed from reported syntheses, are given as procedures 6.A and 6.B, respectively.

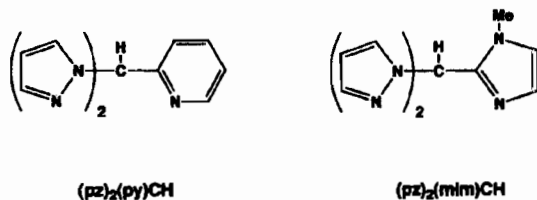


Figure 1. Tripod ligands.

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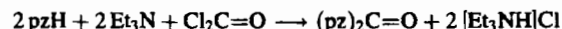
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General Comment

Anaerobic techniques and dry solvents and reagents are used for all preparations.

A. BIS(PYRAZOL-1-YL)METHANONE, (pz)₂C=O



■ **Caution.** Because phosgene is volatile (bp 8°C) and highly toxic by inhalation or skin contact, is a severe lachrymator and is moisture-sensitive, this reaction should be performed in a well-ventilated hood. See general comments for choosing phosgene or related reagents elsewhere in this volume.

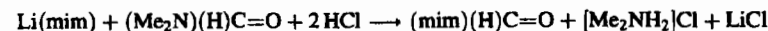
Procedure

Pyrazole (5.0 g, 73.5 mmol, Aldrich) and triethylamine (10.25 mL, 73.5 mmol) are added to diethyl ether (200 mL) in a three-necked 500-mL round-bottomed flask fitted with an overhead stirrer and nitrogen inlet. The mixture is stirred for 5 min using an overhead stirrer. Phosgene (19 mL, 1.93 M in toluene, as received from Fluka) is added in two portions using a pressure equalized dropping funnel. Stirring is continued for 15 min, the precipitate removed by filtration under vacuum, and the volume of the filtrate reduced by rotary evaporation[†] to give a pale yellow oil. Hexane (10 mL) is added and colorless crystals of the product form over 3 h at room temperature or 1 h when cooled in ice. The product is collected by filtration and dried under high vacuum. The yield is 5.65 g (95%).[‡]

Properties

The solid product is unstable at ambient temperature and should be stored at -20°C; mp lit.^{10a} 61.5–62.5°C. ¹H NMR in CDCl₃: δ 8.72 (1H, dd, *J* = 3.1 Hz, H₃), 7.89 (1H, d, *J* = 1 Hz, H₃), 6.54 (1H, dd, *J* = 3.1 Hz, H₄).

B. *N*-METHYLIMIDAZOLE-2-CARBALDEHYDE, (mim)CHO



^{*}The checkers used magnetic stirring with intermittent shaking as needed.

[†]Checkers used cannula filtration and vacuum distillation of solvent.

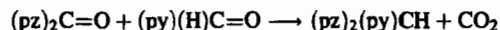
[‡]The checkers report a yield of 76%, m.p. 59–60°C.

Procedure

Butyllithium (140 mL of 1.2 M solution in diethyl ether, 168 mmol, prepared as reported¹¹) is added dropwise to a stirred solution of *N*-methylimidazole (13.4 mL, 168 mmol, Aldrich) in diethyl ether (50 mL) at -80°C in a three-necked 500-mL round-bottomed flask fitted with a nitrogen inlet. The solution is allowed to warm slowly to 0°C , then cooled to -80°C , and added dropwise at this temperature via a jacketed dropping funnel to a mixture of *N,N*-dimethylformamide (25 mL, Aldrich) and diethyl ether (30 mL) stirred with an overhead stirrer at -80°C in a three-necked 500-mL round-bottomed flask fitted with a nitrogen inlet.* The white suspension is allowed to warm to room temperature, and stirred for 6 h, and aqueous HCl (100 mL, 5 M) added dropwise over a few minutes. The organic layer is removed using a separating funnel and washed with 5 M aqueous HCl (2 \times 20 mL). The combined acid extracts are made slightly alkaline with Na_2CO_3 , extracted with dichloromethane (2 \times 40 mL), and the combined extracts are dried over MgSO_4 . After filtration, removal of solvent, and vacuum distillation (60–65 $^{\circ}\text{C}$, 1 torr), the product is obtained as a clear oil that crystallizes on standing (12.8 g, 69%).[†]

Properties

The product should be stored at -20°C . ^1H NMR in CDCl_3 : δ 9.82 (s, 1H, CHO), 7.28 [s, 1H, H(4 or 5)], 7.12 [s, 1H, H(5 or 4)], 4.03 (s, 3H, NMe).

C. BIS(PYRAZOL-1-YL)(PYRIDIN-2-YL)METHANE, (pz)₂(py)CH

Procedure

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and pyridine-2-aldehyde (0.60 mL, 6.3 mmol, Merck) are added to a 50-mL Schlenk tube under nitrogen. A catalytic amount of anhydrous cobalt(II) chloride (0.01 g) is added, although the reaction does proceed satisfactorily without the catalyst. The mixture is gently warmed to $\sim 40^{\circ}\text{C}$ via an external water bath until evolution of carbon dioxide is observed, and the mixture is then cooled and set aside until the reaction has subsided. Water (5 mL) is added and the mixture extracted with dichloromethane

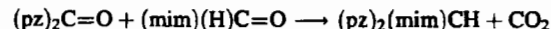
*The checkers used a 1.6 M solution of butyllithium in hexanes (Aldrich) and cannula transfer of DMF/Et₂O solution to the Li(mim) suspension.

[†]The checkers report a yield of 50% at half-scale, crystals at 0°C melting at $\sim 23^{\circ}\text{C}$.

(2 \times 20 mL). The combined extracts are dried over MgSO_4 and filtered, and the solvent is removed in a vacuum.* The product is recrystallized from hot hexane (0.64 g, 45%).

Properties

^1H NMR in CDCl_3 : δ 8.61 [ddd, 1H, H(6)], 7.88 (s, 1H, CH), ~ 7.85 [m, 3H, H(4)_{py} and H(5)_{pz}], 7.42 [ddd, 1H, H(5)_{py}], 7.15 [d, 1H, H(3)_{py}], 6.36 [dd, 2H, H(4)].

D. BIS(PYRAZOL-1-YL)(*N*-METHYLIMIDAZOL-2-YL)METHANE, (pz)₂(mim)CH

Procedure

Bis(pyrazol-1-yl)methanone (0.98 g, 6.3 mmol) and *N*-methylimidazole-2-aldehyde (0.60 mL, 6.3 mmol) are added to a 50-mL Schlenk tube under nitrogen in an open system. A vigorous reaction commences immediately to produce a red-brown tar and carbon dioxide. The material thus obtained is dissolved in dichloromethane and chromatographed on a column ($\sim 2 \times 15$ cm; Merck 60, 230/240-mesh silicagel; 1 atm or medium pressure of nitrogen applied) with dichloromethane used as the eluent. A colorless solution of the product is obtained, as other product(s) are either not eluted or have low R_f values.[†] Addition of hexane (20 mL) to the dichloromethane eluent, followed by slow removal of dichloromethane under a vacuum at room temperature gives (pz)₂(mim)CH as white crystals (1.7 g, 49%).[‡]

Properties

^1H NMR in CDCl_3 : δ 8.00 (s, 1H, CH), 7.93 [d, 2H, H(5)], 7.52 [s, 2H, H(3)], 7.16 [d, 1H, H(4 or 5)_{mim}], 6.87 [d, 1H, H(5 or 4)_{mim}], 3.56 [s, 3H, NMe].

*The checkers monitored purity by thin-layer chromatography (TLC) (silica/Et₂O, product $R_f \sim 0.4$). Hot hexane extract was evaporated, residue extracted with Et₂O, and solution passed over a silica column. Evaporation gave a pale yellow oil that crystallized on standing. Recrystallization from hot hexane cooled to -20°C overnight gave colorless needles in a yield of 30%, mp 78.5–79.0 $^{\circ}\text{C}$.

[†]The checkers found pyrazole in the first fraction eluting.

[‡]The checkers obtained 0.84 g (58% yield, mp 119–120 $^{\circ}\text{C}$) using 13 mg CoCl_2 as catalyst with (pz)₂CO in 2 mL of THF, and adding the solution of (mim)(H)C=O in 2 mL THF by cannula.

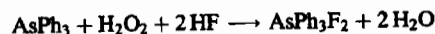
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8. DIFLUOROTRIPHENYLARSENIC(V), AsF₂Ph₃

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Checked by JOHN R. SHAPLEY†



The pentavalent triphenylarsenic dihalides are of interest because they present structures that are dependent on the halogen¹⁻³ and are convenient sources for the preparation of arsenic ylides.^{4,5} The chemistry of triphenylarsenic difluoride,

by far the most air-stable of the halide derivatives, has not been much explored. This is probably because of the synthetic procedures currently available: (1) prolonged heating of triphenylarsine with sulfur tetrafluoride⁶ or (2) halogen exchange between triphenylarsenic dichloride and silver fluoride.⁷ However, we have found that triphenylarsenic difluoride precipitates in good yield when a saturated solution of triphenylarsine oxide in methanol is treated with concentrated hydrofluoric acid. Here we describe a simple one-pot synthesis based on triphenylarsine, that is especially useful when the oxide is not available. It is based in the facile oxidation of triphenylarsine with hydrogen peroxide and the immediate conversion of the oxide into the fluoride.

Procedure

■ **Caution.** Arsenic compounds are poisonous. Concentrated hydrogen peroxide can cause severe burns. Hydrofluoric acid is neurotoxic and corrosive, and causes severe burns. All manipulations should be conducted in an efficient fume hood, and gloves and goggles should be worn.

In a 100-mL Teflon[®] beaker immersed in a bath at 80–100°C are placed 10 g (32.7 mmol) of AsPh₃,[†] 10 g of glacial acetic acid and a magnetic stirring bar. Then 10 g (88.2 mol) of 30% H₂O₂ is added dropwise to the abovementioned mixture with stirring. Some boiling or frothing of the solution may occur, since the reaction is exothermic and oxygen is released. Then 10 g (240 mmol) of 48% HF is added with stirring to the warm solution. During the addition, a white precipitate forms. The beaker is immersed in an ice-cold water bath, and the mixture is stirred for 10 min. Then, 20 g of cold distilled water is added to the mixture and the stirring is continued for further 10 min. The solid product is collected by vacuum filtration, washed with three 5-mL portions of methanol, and dried in air for 10 min. The solid is transferred to a Teflon vial, which is introduced into a round-bottomed flask and maintained under vacuum at room temperature for 2 h. Yield: 10 g (90%).

Anal. Calcd. for AsPh₃F₂: C, 62.81; H, 4.39; F, 11.04. Found: C, 62.6; H, 4.3; F, 11.3.

Properties

White AsF₂Ph₃ melts at 137–139°C. The IR spectrum, taken as a Nujol mull, has the characteristic band ν_{AsF_2} at 517 cm⁻¹. The ¹⁹F NMR spectrum in CDCl₃

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*Similar results are obtained by using a variety of plastic vessels.

†The procedure was checked at half-scale (yield 93%).